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Study of the Low Field Microwave Response in Yttrium Aluminates Dilutely Doped with Manganese

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ABSTRACT

Microwave response near zero magnetic field was observed in $YAlO_3$ and $CaYAlO_4$ crystals dilutely doped with Mn in concentration ranging from 0.05 to 2 atomic %. The response is due to non-resonant microwave absorption, which co-exists with normal electron paramagnetic resonance (EPR) absorption due to different paramagnetic valence states of manganese. Mn^{2+} and Mn^{4+} charge states were identified in Mn-doped $YAlO_3$, and Mn^{2+}, Mn^{4+} and Mn^{5+} in Mn-doped $CaYAlO_4$. The low field response has the opposite phase with respect to the paramagnetic absorption. This shows that Mn-doped $YAlO_3$ and $CaYAlO_4$ exhibit magnetically induced microwave absorption, which has a minimum at zero magnetic field and increases with the applied magnetic field. This effect is similar to microwave magneto-resistance effects observed in manganite perovskites, where spin-dependent electron tunneling occurs between ferromagnetically coupled manganese ions in different valence states. We show, however, that in the present case of diluted paramagnetic systems, magneto-induced microwave losses are due to intramolecular spin-dependent tunneling, where central paramagnetic ion does not change its charge state and spin-dependent charge migration occurs in the first coordination sphere of paramagnetic ion. Evidences are presented that this ion is Mn^{2+} exhibiting the highest electron spin $S = 5/2$.

INTRODUCTION

Recent discoveries of manganese based single molecular magnets, exhibiting magnetization tunneling, inspire the search for manganese doped insulating materials, where similar spin-dependent tunneling may occur within paramagnetic dopant ion and be accompanied by charge displacement current. Since the displacement current is one of the sources of microwave losses in materials, the search for spin-dependent tunneling in insulating materials can be realized through the investigation of their microwave dielectric properties.

Study of microwave dielectric properties of rare-earth aluminates is of interest for their potential applications as dielectric resonators and substrates for high temperature superconductors (HTSC) [1]. In particular, yttrium orthoaluminate $YAlO_3$ was suggested as a substrate material for microstrip antennas utilizing HTSC thin films [1]. Study of the mechanism of the charge carrier mobility is important in understanding of unique dielectric properties of insulators like rare-earth aluminates. $YAlO_3$ doped with manganese has been shown to be a potential material for holographic and data storage [2]. The high holographic recording efficiency in Mn-doped $YAlO_3$ may imply non-centrosymmetric charge distribution. Then microwave properties associated with charge displacement current can be expected in the crystal.

Microwave losses associated with spin-dependent tunneling can be measured by means of microwave response with the applied magnetic field, as it was demonstrated, for example, in manganites [3, 4]. Changes in electron transport characteristics of materials in external magnetic

fields are of great fundamental and practical interests. Externally applied magnetic field may dramatically change properties of the materials from insulators to conductors, for example in manganite perovskites [5-7]. The large magneto-resistance effect in manganite perovskites is presently explained by the enhanced electron hopping migration occurring via double-exchange mechanism in mixed valence Mn^{3+}-O-Mn^{4+} structures and additional magnetic coupling energy that provides ferromagnetism [5]. Thus, magneto-resistance effects are usually considered in materials containing highly concentrated transition metals, as a result of coupling between metal ions in different valence states. Accordingly, microwave magneto-resistance effects have been studied so far in materials containing transition metals as major components.

The purpose of this study is to show that microwave magneto-resistance effects may occur in an insulator dilutely doped with a transition metal. Since there is no possibility for ferromagnetic coupling between largely separated dopant ions, the spin-dependent transport may take place only within a coordination sphere of the paramagnetic dopant ion. In this paper we present the observation of microwave losses induced by low magnetic field in Mn-doped $YAlO_3$ and $CaYAlO_4$.

EXPERIMENTAL DETAILS

Mn-doped $YAlO_3$ and $CaYAlO_4$ crystals were grown by the Czochralski technique in an iridium crucible under nitrogen ambient atmosphere with up to 0.5% of oxygen. 99.999% purity chemicals were used. Manganese in Mn:$YAlO_3$ was introduced in the melt at 0.05 and 0.5 atomic % (with respect to Al) in the form of MnO_2. The crystals were pulled along the *c* direction of the orthorhombic unit cell. The pull rate was maintained at 1.5 mm/h and the rotation rate at 15 rpm. In order to alter manganese valence state, three Mn:$YAlO_3$ crystals were co-doped with cerium in the concentration of 0.05, 0.1 and 0.5% and one crystal was co-doped with cerium and calcium (both dopant concentrations of 0.5%). Cerium and calcium were added in the melt as CeO_2 and $CaCO_3$, respectively. Manganese in Mn:$CaYAlO_4$ was introduced in the melt at 0.1, 0.5 and 2.0% in the form of MnO_2.

Electron paramagnetic resonance (EPR) spectra and microwave losses (non-resonant microwave absorption) of the crystals were recorded by Bruker EMX spectrometer operating at ~9.6 GHz. EPR spectra were recorded at 77 K in liquid nitrogen and in the temperature range 90-300 K using Bruker BVT 3000 liquid nitrogen temperature control system

DISCUSSION

Low field microwave response and EPR of Mn-doped $YAlO_3$

Single crystal and powder sample EPR spectra of Mn:$YAlO_3$ were studied in Ref. [8]. Two paramagnetic charge states of manganese, Mn^{2+} (total electron spin $S = 5/2$) and Mn^{4+} ($S = 3/2$) were identified. Comparison of the ionic radii of dopants and host cations, as well as optical spectroscopic studies [2, 9, 10] show that Mn^{2+} and Mn^{4+} are located in yttrium and aluminum sites, respectively. In this part of the paper we discuss the observation of a new sharp line centered at zero magnetic field in addition to previously observed EPR signal. We have observed this line by sweeping magnetic field through the zero value (zero field crossing) and using considerably higher values of microwave irradiation power (figure 1). As it can be seen from figure 1, the sharp zero field signal has the opposite phase relative to paramagnetic

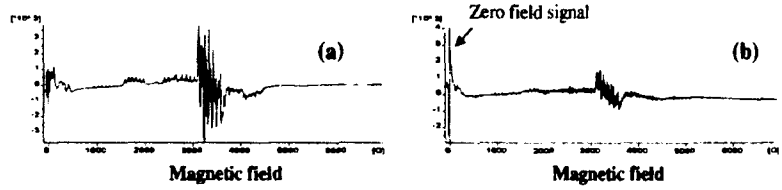

Figure 1. Polycrystalline EPR spectra of 0.5%Mn:$YAlO_3$ recorded at 77 K and different values of microwave power: (**a**) P = 2 mW, (**b**) P = 200 mW.

absorption due to Mn^{2+} and Mn^{4+}. It means that the low field microwave absorption is a minimum at zero field and rapidly increases with the applied magnetic field. This feature of the low field response is similar to the non-resonant microwave absorption commonly observed in HTSC materials, where this absorption may co-exist with normal paramagnetic absorption due to paramagnetic ions.

The following experimental observations further distinguish the zero field microwave response from the resonant paramagnetic absorption. Figure 2 shows the dependence of the signal line amplitudes of the different parts of the overall EPR spectrum upon microwave power and temperature. At 295 K (figure 2, a) with the microwave power P ranging from 0 to 200 mW the zero field signal does not saturate in contrast to the rest of the overall EPR signal, which is a superposition of paramagnetic absorption due to Mn^{2+} and Mn^{4+}. The saturation curve for Mn^{2+} goes through a maximum and then the Mn^{2+} signal decreases at higher microwave power, which is a characteristic of the homogeneously broadened line [11]. The saturation curve for Mn^{4+} shows that its paramagnetic absorption is characterized by inhomogeneously broadened line [11], which can be explained by a slight distribution of spin Hamiltonian parameters for Mn^{4+}. At 77 K the saturation curve for Mn^{4+} signal retains its form of a plateau as it does at 295 K. In the case of Mn^{2+}, the paramagnetic signal rapidly reaches its maximum with increasing the microwave power, and is significantly suppressed down to 20% of the maximal value (figure 2, b). Such significant drop of the Mn^{2+} paramagnetic signal also causes the decrease in the intensity of the zero field response. This implies that the low field microwave absorption is correlated with spin polarization of Mn^{2+}.

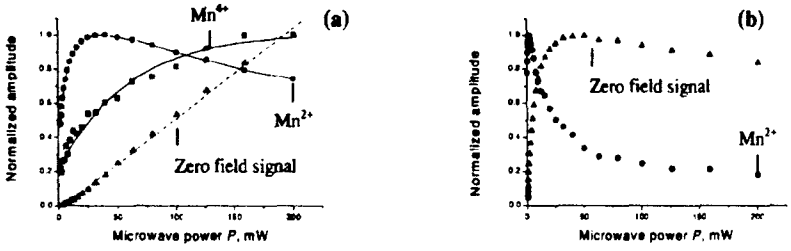

Figure 2. The effect of microwave power P on the EPR and zero field signal amplitudes in 0.5%Mn:$YAlO_3$ at 295 K (**a**) and 77 K (**b**).

It was shown in Ref. [8] that co-doping of the $YAlO_3$ crystal with Ce decreases the amount of Mn^{4+} due to its reduction to Mn^{3+} and results in the disappearance of the Mn^{4+} EPR spectrum. In this crystal we further found that both Mn^{2+} EPR signal and low field response are not affected by the presence of Ce. Co-doping of the $YAlO_3$ crystal with Ca simultaneously increases the EPR signal due to Mn^{2+} ion and the low field microwave response.

Therefore the above data show that the low field microwave response is related to the Mn^{2+} ion, although the response cannot be described as a paramagnetic signal.

Low field microwave response and EPR of Mn-doped $CaYAlO_4$

In the crystal structure of $CaYAlO_4$ [12], aluminum ions are octahedrally coordinated by oxygen atoms. Calcium and yttrium ions are statistically distributed in lattice positions surrounded by nine oxygen atoms. EPR spectra of Mn-doped $CaYAlO_4$ crystals are shown in figure. 3. The reversed phase microwave response centered at zero magnetic field is observed in addition to the normal EPR spectrum with five spectral components (marked with vertical arrows in figure 3, b) of the fine structure due to Mn^{2+} ($S = 5/2$) and some weaker components of the fine structure due to Mn^{4+} ($S = 3/2$). The latter is distinguishable only by the low field part of the three-component fine structure in the EPR spectrum of Mn^{4+}. This feature of the EPR spectrum of Mn^{4+} in $CaYAlO_4$ is similar to that observed for the Mn^{4+} ion in $YAlO_3$ [8] and implies that Mn^{4+} occupies octahedral aluminum site. In the case of $CaYAlO_4$, the EPR spectra show that manganese is predominantly present in the form of Mn^{2+} and, apparently, occupies the Ca^{2+} site with no need for the charge compensation. The orientation dependence of the position of fine structure components of the Mn^{2+} ion, obtained by the two-axis rotation of the crystal in the external magnetic field, is consistent with the tetragonal lattice symmetry of the $CaYAlO_4$ crystal [12]. The central component of the fine structure is related to the spin $-1/2 \leftrightarrow +1/2$ transition and less sensitive to the crystal orientation. It has a distinct six line hyperfine structure due to interaction of the unpaired electron with the ^{55}Mn nucleus (nuclear spin $I = 5/2$). The other components of the Mn^{2+} fine structure exhibit sufficient broadening due to the distribution of zero field splitting parameters, which is the result of the distribution of the crystal field in the disordered Ca^{2+} site in $CaYAlO_4$.

Compared to $Mn:YAlO_3$ crystals, the low field microwave response in $Mn:CaYAlO_4$ is detectable at higher temperatures and lower values of microwave power. Since at the same doping level of manganese in both crystals the amount of Mn^{2+} ions in $Mn:CaYAlO_4$ is much greater than in $Mn:YAlO_3$, we can conclude that the low field microwave response is due to Mn^{2+}. Moreover, the shape of the low field microwave response is identical in both crystals, although the zero field splitting parameters for Mn^{2+} are different by an order of magnitude.

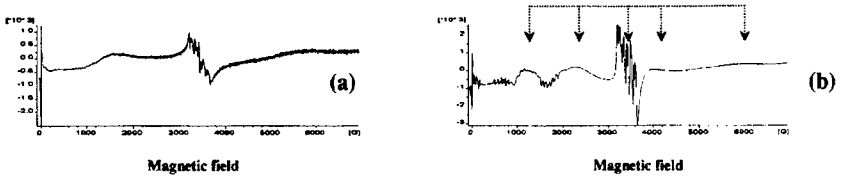

Figure 3. EPR spectra of 0.5%$Mn:CaYAlO_4$ recorded at 77 K and $P = 200$ mW for polycrystalline sample **(a)**, and single crystal **(b)**. The single crystal was oriented such that ***c*** and ***a*** crystal axes were respectively perpendicular and parallel to the external static magnetic field.

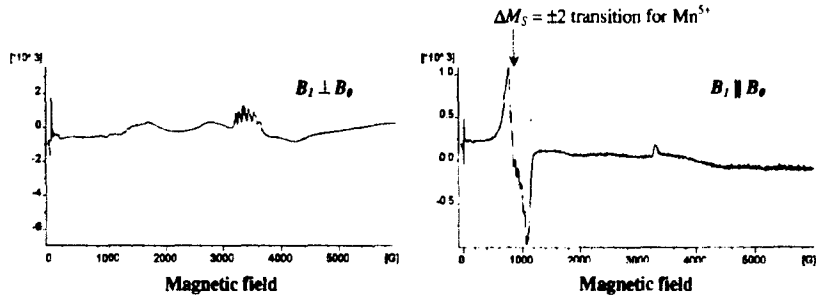

Figure 4. Single crystal EPR spectra of 0.5%Mn:$CaYAlO_4$ recorded at 90 K, P = 200 mW with normal ($B_1 \perp B_0$) and parallel ($B_1 \parallel B_0$) polarization of microwave field. Crystal orientation was as follows: $c \perp B_0$, $a \wedge B_0 = 40°$.

In figure 4, we compare single crystal EPR spectra of Mn-doped $CaYAlO_4$ that were recorded using normal polarization ($B_1 \perp B_0$) of the magnetic component of microwave B_1 with respect to static external magnetic field B_0, and parallel polarization ($B_1 \parallel B_0$). Normal polarization detects allowed $\Delta M_S = \pm 1$ spin transitions. These transitions are not usually seen for manganese charge states with integer electron spin, e.g. Mn^{3+} ($S = 2$) and Mn^{5+} ($S = 1$), while in some cases these ions can be identified by parallel polarization that detects "forbidden" $\Delta M_S = \pm 2$ transitions. We observed this transition (figure 4) in Mn-doped $CaYAlO_4$ single crystal. The crystal orientation dependence analysis of this transition shows that it is due to Mn^{5+}.

Experimental details and results on EPR of Mn^{5+} in $CaYAlO_4$ will be reported elsewhere. However, at this stage of our discussion we refer to figure 4 and note that the low field microwave response (zero field signal) is not sensitive to mutual orientations of microwave and static magnetic fields as much as resonant paramagnetic absorption. This finding confirms the non-resonant nature of the low field microwave absorption.

Model of spin-dependent charge migration in the vicinity of Mn^{2+} as a source of magnetically induced microwave losses

The presence of non-resonant absorption in $YAlO_3$ and $CaYAlO_4$ with the concentration of Mn as low as 0.1% does not allow assumptions about ferromagnetic or exchange coupling between manganese ions with different charge states, that were used for explanation of magneto-resistance in manganite perovskites [5-7]. Therefore, the observed effect cannot be related to changes in d.c. conductivity of the yttrium aluminates, but should be considered as the enhancement of microwave dielectric losses associated with charge displacement current.

Based on local non-centrosymmetric environment of Mn ions in $YAlO_3$ [2], we assume that coordination sphere of Mn^{+2} ion is characterized by a non-zero electric dipole moment due to partially covalent bond, $Mn^{+2-\delta}$–$O^{-2+\delta}$, between manganese and one of the oxygen atoms in its coordination sphere. If the external magnetic field is applied, it will reduce fluctuation of unpaired electron spins and align them in one direction, so that electron can tunnel from one oxygen atom to another without the change of the total spin of the system.

$$O^{-2}(\uparrow\downarrow)...Mn^{+2-\delta}(\uparrow\uparrow\uparrow\uparrow...\uparrow\downarrow...\uparrow)O^{-2+\delta} \rightarrow O^{-2+\delta}(\uparrow...\uparrow\downarrow...\uparrow\uparrow\uparrow\uparrow)Mn^{+2-\delta}...O^{-2}(\uparrow\downarrow) \qquad (1)$$

In this case the dielectric loss will increase due to the additional tunneling migration of the charge $+\delta$. This additional transfer mechanism exists via *p-d* exchange type integral between Mn and O atoms described by Anderson and Hasegawa [13]. Further studies on the low field microwave absorption in diluted paramagnetic systems will be performed in near future to develop a quantitative model of spin-dependent tunneling (1).

CONCLUSIONS

We have observed magneto-induced non-resonant microwave absorption caused by dilutely dissolved paramagnetic manganese ions in insulating $YAlO_3$ and $CaYAlO_4$ crystals. This phenomenon is described in terms of spin-dependent dielectric loss or microwave magneto-resistance that derives from the tunneling charge migration between oxygen atoms via the Mn^{2+} ion exhibiting the highest effective electron spin $S = 5/2$. The spin-dependent tunneling described in the present work results in a distinct, detectable response in the low magnetic field region, which makes Mn-doped insulating yttrium aluminates potential materials for spin electronics.

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